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# DESIGNING THE ULTIMATE PHOTORESIST

by

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## ABSTRACT

This paper will explore two methodologies, point optimization and path optimization, as means for judging, and thus improving, the quality of a photoresist process. The point optimization method examines one point in space and determines what photoresist and aerial image properties maximize performance at this one point. The path optimization technique use a more realistic approach by optimizing over the path of dissolution rather than at one point. The result is a set of criterion which can be used to judge, in some limited respect, the lithographic quality of a photoresist, thus providing a useful tool for designing the ultimate photoresist.

## INTRODUCTION

“If I only had a better stepper,” the resist engineer laments, “then I could use the full potential of my new photoresist.”

“If I only had a great resist,” replies the stepper engineer, “then I could really push the limits of this tool.”

The question of resist improvement versus image improvement has long been a tricky one. Which technology is limiting my performance the most? Which should I concentrate my efforts on? If I had the perfect lithographic tool, how good would my resist be? If I had the ultimate resist, how good would my tool perform? These questions are not easily answered. In the first place, what is a “perfect” imaging tool, and what is the “ultimate” photoresist? This paper will begin to address the latter question.

On the surface, the question of what makes a photoresist good is easily answered: high contrast. But this measure, as will be shown, does not give a complete picture of the influence of the photoresist on the imaging process even when properly defined and used. Instead, a more complete description of the development process, coupled with a simple knowledge of the aerial images used, will lead to other measures of resist performance.

This paper will begin with a review of a well established photoresist optimization methodology called *point optimization*<sup>1</sup>. In this methodology, one point in space is chosen (usually the nominal line

edge) and then all aspects of the process are optimized with respect to this point. The result is a simple and straightforward approach to defining metrics for the quality of each step in the process. Point optimization, however, is by its very nature limiting since only one point in space is considered. Thus, any interesting and important phenomena which might occur elsewhere are neglected. A more complete description of the process would employ *path optimization*, which will be introduced in this paper. In this method, the behavior of the photoresist over the path of dissolution is considered and optimized.

## ABSORPTION AND EXPOSURE FUNDAMENTALS

The basic law of absorption is an empirical one with no known exceptions. It was first expressed by Lambert in differential form as

$$\frac{dI}{dz} = -\alpha I \quad (1)$$

where  $I$  is the intensity of light traveling in the  $z$ -direction through a medium, and  $\alpha$  is the absorption coefficient of the medium and has units of inverse length. In a homogeneous medium (i.e.,  $\alpha$  is not a function of  $z$ ), equation (1) may be integrated to yield

$$I(z) = I_0 \exp(-\alpha z) \quad (2)$$

where  $z$  is the distance the light has traveled through the medium and  $I_0$  is the intensity at  $z=0$ .

In 1852 Beer showed that for dilute solutions the absorption coefficient is proportional to the concentration of the absorbing species in the solution.

$$\alpha_{\text{solution}} = ac \quad (3)$$

where  $a$ , the molar absorption coefficient, =  $\alpha MW/\rho$ ;  $MW$  is the molecular weight;  $\rho$  is the density; and  $c$  is the concentration. The stipulation that the solution be dilute expresses a fundamental limitation of Beer's Law. At high concentrations, where absorbing molecules are close together, the absorp-

tion of a photon by one molecule may affect the ability of another molecule to absorb light. Since this interaction is concentration dependent, it causes deviation from the linear relation (3). Also, an apparent deviation from Beer's law occurs if the index of refraction changes appreciably with concentration (resulting in measurement errors which are difficult to distinguish from a change in absorption).

For an  $N$  component homogeneous solid, the overall absorption coefficient becomes

$$\alpha_T = \sum_{j=1}^N a_j c_j \quad (4)$$

We can now apply the concepts of macroscopic absorption to a typical positive photoresist. A diazonaphthoquinone positive photoresist (such as AZ1350J) is made up of four major components; a base resin  $R$  which gives the resist its structural properties, a photoactive compound  $M$  (abbreviated PAC), exposure product  $P$  generated by the reaction of  $M$  with ultraviolet light, and a solvent  $S$ . Although photoresist drying during prebake is intended to drive off solvents, thermal studies have shown that a resist may contain 10% solvent after a 30 min 100°C prebake<sup>2,3</sup>. The absorption coefficient  $\alpha$  is then

$$\alpha = a_M M + a_P P + a_R R + a_S S \quad (5)$$

If  $M_0$  is the initial PAC concentration (i.e., with no UV exposure), the stoichiometry of the exposure reaction gives

$$P = M_0 - M \quad (6)$$

Equation (5) may be re-written as<sup>4</sup>

$$\alpha = Am + B \quad (7)$$

where  $A = (a_M - a_P)M_0$   
 $B = a_P M_0 + a_R R + a_S S$   
 $m = M/M_0$

The quantities  $A$  and  $B$  are experimentally measurable<sup>4</sup> and can be easily related to typical resist

absorbance curves, measured using an UV spectrophotometer. When the resist is fully exposed,  $M=0$  and

$$\alpha_{\text{exposed}} = B \quad (8)$$

Similarly, when the resist is unexposed,  $m = 1$  ( $M = M_0$ ) and

$$\alpha_{\text{unexposed}} = A + B \quad (9)$$

From this  $A$  may be found by

$$A = \alpha_{\text{unexposed}} - \alpha_{\text{exposed}} \quad (10)$$

Thus,  $A(\lambda)$  and  $B(\lambda)$  may be determined from the UV absorbance curves of unexposed and completely exposed resist.

On a microscopic level, the absorption process can be thought of as photons being absorbed by an atom or molecule causing an outer electron to be promoted to a higher energy state. This phenomenon is especially important for the photoactive compound since it is the absorption of UV light which leads to the chemical conversion of  $M$  to  $P$ .



This concept is stated in the first law of photochemistry: only the light which is absorbed by a molecule can be effective in producing photochemical change in that molecule.

The influence of light intensity on the above chemical reaction is explicitly accounted for in the kinetic rate equation for the reaction.

$$\frac{dm}{dt} = -CI m \quad (12)$$

where  $I$  is the intensity of light striking the photoactive compound,  $t$  is the exposure time, and  $C$  is the rate constant. The influence of light absorption is implicitly accounted for in the rate constant. By applying the theories of microscopic absorption, the rate constant  $C$  can be related to the molar

absorptivity of the photoactive compound  $a_M$  and the quantum efficiency of the reaction,  $\phi^5$ .

$$C = \frac{a_M \lambda \phi}{N_A h c} \quad (13)$$

where  $N_A$  is Avogadro's number,  $h$  is Planck's constant,  $c$  is the speed of light in vacuum, and  $\lambda$  is the vacuum wavelength of the exposure radiation. The quantum efficiency is defined as the number of product molecules produced per photon absorbed by  $M$ .

If the intensity is constant over time, the rate equation (12) can be integrated to solve for the relative PAC concentration as a function of exposure.

$$m = e^{-Ct} \quad (14)$$

From the above equations, one can come to some simple conclusions on how to optimize a photoresist based on the ill defined concept of "sensitivity." It would be desirable to affect a given chemical change (i.e., a given value of  $m$ ) with the least amount of exposure dose. From equation (14) above, it is clear then that a high value of the exposure rate constant  $C$  is needed. Examining the nature of this constant in equation (13) shows that, ignoring wavelength, only two variables are under the control of the resist designer: the molar absorptivity of the PAC and the quantum efficiency. Obviously, a quantum efficiency of 1 is optimum since in this case every photon absorbed by the PAC causes chemical conversion. Increasing  $a_M$ , however, is not as obvious a choice. Although a higher molar absorptivity will increase  $C$ , it will also increase  $A$  (see equation (7)) resulting in higher absorption. Higher absorption, in turn, results in a higher required exposure dose in order to ensure proper exposure of the bottom of the photoresist. There will be, in general, an optimum value of the molar absorptivity in order to minimize the required exposure dose, although this optimum will depend on both the thickness of the resist and the required level of exposure (i.e., value of  $m$ ) to produce the proper imaging. Unfortunately, both  $a_M$  and  $\phi$  are functions of the molecular structure of the PAC and are not readily changeable for any given general resist chemistry.

## OPTIMIZATION AT A POINT: THE LOG-SLOPE METHOD

Full optimization of a lithographic process requires thorough and time consuming calculations of many effects. One simplified approach to this optimization problem is to perform limited calculations at one point in space, say at a point in the resist corresponding to the nominal line edge, and try to optimize certain important properties of the resist feature at this point. Such a point optimization method, by its very nature, is somewhat limiting since any interesting and important lithographic effects which occur elsewhere in the photoresist are not accounted for. However, if the point used is of interest (such as the nominal line edge) and the method used has physical significance, the results can be very useful.

In this section, the log-slope method introduced earlier<sup>1,6-9</sup> will be reviewed as an appropriate point optimization method for maximizing exposure latitude through focus.

### Aerial Image

To simplify the analysis of a lithographic process, it is highly desirable to separate the effects of the lithographic tool from those of the photoresist process. This can be done with reasonable accuracy only if the interaction of the tool (i.e., the aerial image) with the photoresist is known. Consider an aerial image of relative intensity  $I(x)$  where  $x$  is the horizontal position (i.e., in the plane of the wafer and mask) and is zero at the center of a symmetric mask feature. The aerial image exposes the photoresist to produce some chemical distribution  $m(x)$  within the resist. This distribution is called the *latent image*. Many important properties of the lithographic process, such as exposure latitude and development latitude, are a function of the gradient of the latent image  $\partial m/\partial x$ . Larger gradients result in improved process latitude. By taking the derivative of equation (14), it can be shown that the latent image gradient is related to the aerial image by<sup>1</sup>

$$\frac{\partial m}{\partial x} = m \ln(m) \frac{\partial \ln I}{\partial x} \quad (15)$$

where the logarithmic slope of the aerial image is often called just the *log-slope*. The development properties of the photoresist translate the latent image gradient into a development gradient, which then allows for the generation of a photoresist image. Optimum photoresist image quality is obtained with a large development rate gradient. A lumped parameter called the photoresist contrast,  $\gamma$ , can be defined that relates the aerial image and the development rate,  $r$  (see Appendix A for a derivation):

$$\frac{\partial \ln r}{\partial x} = \gamma \frac{\partial \ln I}{\partial x} \quad (16)$$

Equation (16) is called the *lithographic imaging equation* and shows in a concise form how a gradient in aerial image intensity results in a solubility differential in photoresist. The development rate gradient is maximized by higher resist contrast and by a larger log-slope of the aerial image.

The above discussion clearly indicates that the aerial image log-slope is a logical metric by which to judge the quality of the aerial image. In particular, the image log-slope, when normalized by multiplying by the feature width, is directly proportional to exposure latitude expressed as a percent change in exposure to give a percent change in linewidth. This normalized log-slope (*NLS*) is given by

$$NLS = w \frac{\partial \ln I}{\partial x} \quad (17)$$

This metric was first discussed by Levenson, et al.,<sup>10</sup> and later in a related form by Levinson and Arnold<sup>11,12</sup>, before being explored to great extent by this author<sup>6-9</sup>.

### Focus and the Aerial Image

Shown in Figure 1 is the well known effect of defocus on the aerial image. Both the edge slope of the image and the center intensity decrease with defocus, and the intensity at the mask edge remains nearly constant or increases slightly. To compare aerial images using the log-slope, one must pick an  $x$ -value to use. An obvious choice is the mask edge (or more correctly, the nominal feature edge). Thus, all subsequent reference to the slope of the log-aerial

image will be at the nominal feature edge. Now the effect of defocus on the aerial image can be expressed by plotting log-slope as a function of defocus, as shown in Figure 2. The log-slope defocus curve has proven to be a powerful tool for understanding focus effects and is used extensively in this paper.

Some useful information can be obtained from a plot of log-slope versus defocus. As was previously discussed, exposure latitude varies directly with the log-slope of the image. Thus, a minimum acceptable exposure latitude specifications translates directly into a minimum acceptable value of the NLS. The log-slope versus defocus curve then can be used to give a maximum defocus to keep the process within this specification. If, for example, the minimum acceptable normalized log-slope of a given process was determined to be 3.5, the maximum defocus of 0.5 $\mu$ m lines and spaces on a 0.53 NA i-line stepper would be, from Figure 2, about  $\pm 0.8\mu$ m. This gives a practical definition of the depth-of-focus that separates the effects of the aerial image and the photoresist process. The printer determines the shape of the log-slope defocus curve, and the process determines the range of operation (i.e., the minimum NLS value). If the minimum log-slope needed was 6, one would conclude from Figure 2 that this printer could not adequately resolve 0.5 $\mu$ m lines and spaces. Thus, resolution can also be determined from a log-slope defocus curve.

To define resolution, consider Figure 3, which shows the effect of feature size on the log-slope defocus curve. If, for example, a particular photoresist process requires a NLS of 3.8, one can see that the 0.4 $\mu$ m features will be resolved only when in perfect focus, the 0.5 $\mu$ m features will have a DOF of  $\pm 0.7\mu$ m, and the 0.6 $\mu$ m features will have a DOF of  $\pm 0.9\mu$ m. Obviously, the DOF is extremely sensitive to feature size, a fact that is not evident in the common Rayleigh definition. Since DOF is a strong function of feature size, it is logical that resolution is a function of the required DOF. Thus, in the situation shown in Figure 3, if the minimum acceptable DOF is  $\pm 0.8\mu$ m and the required NLS is

3.8, the practical resolution is about 0.55 $\mu$ m for equal lines and spaces. Resolution and depth-of-focus cannot be independently defined, but rather are interdependent. To summarize, depth-of-focus can be defined as the range of focus which keeps the log-slope above some specification for a given feature. Resolution can be defined as the smallest feature which keeps the log-slope above some specification over a given range of focus.

The key to the above definitions for resolution and depth-of-focus is the linear correlation between the NLS and exposure latitude. But in order to make quantitative estimates, one must have a reasonable estimate for the minimum acceptable normalized log-slope. How is such an estimate obtained? By measuring a focus exposure matrix, one can obtain an experimental plot of exposure latitude versus defocus. This can be repeated for many different feature types and sizes, if desired. Figure 4a shows an example of such a plot where exposure latitude (*EL*) is defined as the range of exposure (as a percentage of the nominal dose) which keeps the linewidth within  $\pm 10\%$  of the nominal. Obviously, exposure latitude decreases greatly as the image is defocused. By comparing such experimental data with the log-slope defocus curves as in Figure 3, a correlation between NLS and exposure latitude can be obtained. In this case, the data in Figures 3 and 4a are correlated by the simple expression

$$EL = 8.1(NLS - 1.1) \quad (18)$$

Figure 4b shows the goodness of the fit given by equation (18). Note that the smallest feature begins to deviate from this fit, indicating a non-linear resist response below some feature size (this is directly analogous to the concept of the film MTF often used in the photographic sciences).

Equation (18) in and of itself leads to very revealing interpretations. First, note that a NLS of at least 1.1 must be used before an image in photoresist is obtained even at one exposure level. Above a NLS of 1.1, each increment in NLS adds 8.1% exposure latitude. Finally, if a minimum required exposure

latitude is specified for a process, this value will translate directly into a minimum required NLS. For example, if an *EL* of 20% is required, the NLS which just achieves this level is 3.6. Thus, all images with a NLS in excess of 3.6 would be considered acceptable from an exposure latitude point of view. Correlations like equation (18) are very process dependent. However, for a given process such a correlation allows imaging parameters to be studied by simply examining the log-slope defocus behavior.

The log-slope defocus curve can now be used to explore the effects of various parameters on the resolution and depth-of-focus. The numerical aperture is one of the most important parameters defining lithographic performance, and yet it is the most misunderstood. The Rayleigh DOF equation seems to predict a dramatic decrease in DOF with increasing numerical aperture. Shown in Figure 5 is the effect of numerical aperture on the log-slope defocus curve of 0.5 $\mu\text{m}$  lines and spaces. The effect of increasing NA is to improve the aerial image log-slope when small amounts of defocus are present, and worsen the log-slope of an image with larger amounts of defocus. This is an extremely important result. Increasing the numerical aperture will improve image quality only if focus errors can be kept below a certain value. In fact, for a given amount of defocus, there is an optimum NA that gives the largest log-slope. Similarly, for a given log-slope specification, there will be one NA which maximizes the depth-of-focus.

The role of wavelength in depth-of-focus is also misunderstood. Although the Rayleigh criterion seems to indicate worse DOF with shorter wavelength, Figure 6 shows that DOF improves as wavelength decreases for a given feature size. Figures 5 and 6 show clearly the danger of using the Rayleigh criterion for comparing the DOF of different printers (i.e., different values of wavelength and numerical aperture).

The log-slope defocus curve can be used objectively to compare different printers. Recently there has been much discussion on the advantages of

shorter wavelength versus higher numerical aperture. For example, one could compare an i-line, 0.53 NA system with a deep-UV 248nm, 0.36 NA system. Both have the same value of  $\lambda/NA$  and thus, according to the Rayleigh criterion, the same resolution. In terms of the log-slope curve, the same value of  $\lambda/NA$  corresponds to the same value of the log-slope of the image with no defocus (Figure 7). The practical resolution is defined as the smallest feature meeting a given log-slope specification over a given focus range. If a process requires a normalized log-slope of 3.5 and a focus budget of  $\pm 1\mu\text{m}$ , Figure 7 shows that the deep-UV system will resolve the 0.5 $\mu\text{m}$  feature, but the i-line system will not. Thus, the shorter wavelength system has better practical resolution than the i-line system even though  $\lambda/NA$  is the same for the two printers.

It is important to note that all of the aerial image calculations presented in this paper assume diffraction-limited lens performance, i.e., ideal lenses. Obviously, the ideal lens does not exist, and thus real lenses have log-slope versus defocus curves that are degraded to some extent from the ideal curves shown here. When comparing different lenses, as was done above, one must keep in mind that one lens may be farther from the ideal than the other. Of course, if the amount of aberrations for a given lens is known, these aberrations can be included in the calculation of log-slope.

Other image-related parameters can be easily studied using the log-slope defocus curves. The differences between imaging dense and isolated features, or lines versus contacts, for example, can be examined. Partial coherence effects can be evaluated. The log-slope defocus approach has been used to optimize the numerical aperture and partial coherence of a stepper<sup>13</sup>, examine the differences between imaging in positive and negative tone resist<sup>14</sup>, and study the advantages of off-axis illumination<sup>15</sup>.

Although defocus is strictly an optical phenomenon, the photoresist plays a significant role in determining the effects of defocus. As one might imagine, a better photoresist will provide greater

depth-of-focus. In light of the above description of defocus using log-slope defocus curves, the photoresist impacts the DOF by changing the minimum acceptable log-slope specification. A better photoresist will have a lower log-slope specification, resulting in a greater usable focus range. This relationship between the photoresist and the log-slope specification is determined experimentally as described above by measuring exposure latitude versus defocus. In general, the resulting correlation between the normalized log-slope (*NLS*) and the exposure latitude (*EL*) is given by

$$EL = \alpha (NLS - \beta) \quad (19)$$

where  $\beta$  is the minimum *NLS* required to given any image at all in photoresist, and  $\alpha$  is the percent increase in exposure latitude per unit increase in *NLS*. Thus, to a first degree, the effect of the photoresist on depth-of-focus can be characterized by the two parameters  $\alpha$  and  $\beta$ .

Consider for a moment an ideal, infinite contrast photoresist. For such a case, the slope of the exposure latitude curve will be exactly  $2/NLS$ <sup>16</sup> (see Appendix B for a derivation). Thus, using a typical linewidth specification of  $\pm 10\%$ , an infinite contrast resist would make  $\alpha=10$  and  $\beta=0$ . The quality of a photoresist with respect to focus and exposure latitude can be judged by how close  $\alpha$  and  $\beta$  are to these ideals.

## Exposure Optimization

In justifying the use of the log-slope as a metric for the quality of the aerial image, it was mentioned that the aerial image log-slope was directly related to the gradient of exposed photoresist. The latent image  $m(x,y,z)$  is given in the simplest case by equation (14). Thus, to find the gradient of the latent image, one need only differentiate this equation to obtain equation (15). Several very interesting and important conclusions can be drawn from this simple equation. First, the slope of the latent image is not proportional to the slope of the aerial image, but to the slope of the log-aerial image. This dependency has been discussed previ-

ously<sup>1</sup> and will be shown to be important in nearly every aspect of lithographic imaging. Further, for a given aerial image, the slope of the latent image is a function of exposure. By plotting  $m \ln(m)$ , one can see that there is one value of  $m$  which gives a maximum latent image slope (Figure 8). It is easily determined that the maximum occurs at

$$m = e^{-1} \approx 0.37 \quad (20)$$

Thus, there is only one exposure energy which will maximize the latent image slope at some position  $x$  (e.g., at the mask edge), that which gives  $m(x)$  equal to 0.37. The implications of this result are very important. First, there is one and only one exposure energy which gives the optimum latent image. Since, as will be shown later, process latitude is a function of the latent image slope, varying the exposure will vary the latitude of a photolithographic process.

Equation (15) actually only applies to the top of the resist, or for a resist with no bleaching ( $A=0$ ) since the original equation (14) applies only to these cases. A more detailed analysis is given in Appendix C which includes the effects of photoresist bleaching. The result is shown in Figure 9. Over a wide range of values of  $A$  times depth into the resist ( $Az$ ), the optimum PAC slope is obtained for values of  $m$  in the range of 0.35 to 0.37. As can be seen, the PAC gradient is improved for larger bleaching effects (larger  $A$ ). This has been referred to as the "built-in contrast enhancement effect" of resist bleaching.

One can see from Figure 9 that the maximum of the PAC gradient is fairly broad. Although the exact maximum may be about 0.37, the gradient is within 10% of the maximum over the range of about 0.2 to 0.5. For practical reasons it will be preferable to work with higher values of  $m$  (i.e., lower exposures), such as  $m=0.5$  at the mask edge.

It is clear from the above discussion that the exposure dose plays an important role in determining the quality of the resulting latent image and that there is one dose which will give the optimum latent



Consider an average range of exposure doses resulting from the aerial image of 4X (i.e., the highest dose is four times the dose at the line edge). This range of doses can be superimposed on the resist contrast curve as shown in Figure 12. As can be seen, this range of exposure doses will result in a range of development rates. The high dose, corresponding to the energy in the center of a space, results in a high development rate, and the lowest dose, corresponding to the nominal line edge, results in a low development rate. It seems intuitive that one would want a maximum ratio of high to low development rates in order to get good imaging. In fact, this statement can be proven theoretically<sup>1</sup>. By sliding this 4X range along the exposure dose axis, it is fairly easy to find the position which results in the maximum development rate ratio. Since the upper end of the exposure dose range corresponds roughly to the nominal exposure dose, this position of the range will then determine the optimum nominal exposure dose. As a result, a knowledge of the contrast curve of a given photoresist process will allow easy determination of the optimum exposure dose. Proper linesize is obtained by adjusting the development time.

The above methodology can be used to find the optimum dose for any given contrast curve. Thus, two different resists (or different resist processes) can be compared by determining which gives the greatest development rate ratio at the optimum exposure conditions. Thus, rather than comparing resists at one point, the normal range of operation of the resists are compared.

The above path optimization technique is a simple one. More rigorous path optimization methods can be envisioned which include not only the development rate along the path due to the aerial image variation, but also the direction of the path into the photoresist to include variations in development rate as a function of absorption and standing waves. Although the mathematics of such calculations can become complex, they can be accommodated by computer simulations quite readily. Thus, future work in this area would apply rigorous path calculations to determine in the influence of the develop-

ment rate versus energy on the resulting lithographic patterns.

## CONCLUSIONS

This paper presented a review of the well established photoresist optimization technique of point optimization. In this methodology, one point in space is chosen (usually the nominal line edge) and then all aspects of the process are optimized with respect to this point. The result is a simple and straightforward approach to defining metrics for the quality of each step in the process. The limitations of point optimization were also described. A more complete description of the process employing path optimization was introduced in this paper. In this method, the behavior of the photoresist over the path of dissolution is considered and optimized. One simple path optimization technique was presented in which a known range of exposure is adjusted to maximize the resulting range in development rate. As a result, the nominal exposure dose can easily be optimized and different resists or processes can be readily and objectively compared. Using this technique as a tool, photoresist designers can compare resist designs and formulations where slight variations in the shape of the development rate versus energy contrast curve result, making the design of the ultimate photoresist more likely.

## APPENDIX A

The use of "contrast" to describe the response of a photosensitive material dates back over one hundred years. Hurter and Driffield measured the optical density of photographic negative plates as a function of exposure<sup>17</sup>. The "perfect negative" was one which exhibited a linear variation of optical density with the logarithm of exposure and a plot of optical density versus log-exposure showed that a good negative exhibited a wide "period of correct representation." Hurter and Driffield called the slope of this curve in the linear region  $\gamma$ , the "development constant." Negatives with high values of  $\gamma$  were said to be "high contrast" negatives because the photosensitive emulsion quickly changed from low to high optical density when exposed. Of course,

high contrast film is not always desirable since it easily saturates.

Photolithography evolved from photographic science and borrowed many of its concepts and terminology. When exposing a photographic plate, the goal is to change the optical density of the material. In lithography, the goal is to change the development rate of the photoresist. Thus, the analogous H-D curve for lithography plots log-development rate versus log-exposure. Following the definition of  $\gamma$  from Hurter and Driffield, the photoresist “contrast” can be defined as

$$\gamma \equiv \frac{\partial \ln R}{\partial \ln E} \quad (\text{A-1})$$

where  $R$  is the resist development rate and  $E$  is the exposure energy. Note that this definition of contrast has been called the *theoretical contrast* by the author<sup>1,18</sup> to distinguish it from the often misquoted measured contrast based on the photoresist “contrast curve” of resist thickness remaining versus log-exposure dose.

The goal of lithographic exposure is to turn a gradient in exposure energy (an aerial image) into a gradient in development rate. Since intensity  $I$  and energy are related by a constant (the exposure time),  $\partial \ln E = \partial \ln I$ . Thus, from equation (A-1) it is very easy to express the development rate gradient as<sup>1,18</sup>

$$\frac{\partial \ln R}{\partial x} = \gamma \frac{\partial \ln I}{\partial x} \quad (\text{A-2})$$

where  $x$  is the horizontal distance from the center of the feature being printed. The left hand term is the spatial gradient of development rate. To differentiate between exposed and unexposed areas, it is desirable to have this gradient as large as possible. The right hand side of equation (A-2) contains the log-slope of the aerial image. This term represents the quality of the aerial image, or alternatively the amount of information contained in the image about the position of the mask edge. The photoresist contrast “amplifies” the information content of the image and transfers it into the photoresist as a development rate gradient. This expression quite clearly illustrates the role of contrast in defining the “goodness” of a photoresist process.

## APPENDIX B

The relationship between the normalized log-slope of the aerial image (NLS) and exposure latitude has been discussed before<sup>16</sup> and will be briefly reviewed here. Consider, in the limiting case, an ideal “threshold” photoresist, one that has a high development rate for exposure energies above some  $E_{th}$  and zero development rate for energies below this value. For such a case, the linewidth ( $w$ ) formed upon exposure to some aerial image  $I(x)$  will be determined by the nominal exposure dose ( $E$ ) and the spatial intensity variation of the image. That is,

$$EI(w/2) = E_{th} \quad (\text{B-1})$$

To determine how linewidth varies with exposure dose, one simply has to take the derivative of this equation.

$$2 \frac{\partial \ln E}{\partial w} = - \frac{\partial \ln I}{\partial x} \quad (\text{B-2})$$

Ignoring the sign and normalizing by multiplying both sides of the equation by the linewidth,

$$2 \frac{\partial \ln E}{\partial \ln w} = NLS \quad (\text{B-3})$$

This final equation tells us that, for an ideal threshold photoresist, the slope of an exposure latitude curve (log-linewidth versus log-exposure dose) will be  $2/NLS$ . We can interpret  $\partial \ln E$  as a percent change in exposure and  $\partial \ln w$  as the resulting percent change in linewidth. Assuming a typical linewidth specification for  $\partial \ln w$  would allow the term  $\partial \ln E$  to be interpreted as the exposure latitude ( $EL$ ), the percent change in exposure which keeps the linewidth within specification. Letting this linewidth specification be  $\pm 10\%$  (for a total range of 20%), the ideal exposure latitude would be given by

$$EL = 10 NLS \quad (\text{B-4})$$

A real (non-ideal) photoresist would have an exposure latitude less than this amount.

## APPENDIX C

The exposure of diazo-type novolak based positive photoresists can be described mathematically using the kinetics of the exposure reaction. The result is the well known first order rate equation,

$$\frac{\partial m}{\partial t} = -CIm \quad (C-1)$$

where  $m$  is the relative concentration of unexposed photoactive compound (PAC),  $I$  is the intensity of the exposing radiation within the resist,  $C$  is a rate constant, and  $t$  is the exposure time. The variables  $I$  and  $m$  are considered to be functions of two dimensions (in the simplest case):  $x$ , the horizontal position; and  $z$ , the depth into the photoresist. The point  $x=0$  is arbitrarily set as the center of a symmetric mask feature and  $z=0$  is the top of the resist. Equation (C-1) can be solved quite easily for the case of constant intensity, that is, when the photoresist does not bleach during exposure. The more general case requires more information about the intensity. The simplest case is when the photoresist is coated on a non-reflecting substrate so that the variation of  $I$  with depth into the resist is given by the Lambert-Beer law:

$$\frac{\partial \ln(I)}{\partial z} = -(Am + B) \quad (C-2)$$

where  $A$  and  $B$  are constants which have been defined previously. Equations (C-1) and (C-2) form two coupled partial differential equations with the following boundary conditions:

$$\begin{aligned} I(x, 0) &= I_0 \\ m(x, 0) &= m_0 \end{aligned} \quad (C-3)$$

One can also see that these two boundary values are related by

$$m_0 = e^{-Ct_0} \quad (C-4)$$

since  $I_0$  does not change with time.

Equations (C-1) and (C-2) with boundary conditions (C-3) can be solved exactly<sup>19</sup> with the solution taking the form of an integral:

$$z = \int_{m_0}^m \frac{dy}{y[A(1-y) - B\ln(y)]} \quad (C-5)$$

where  $y$  is a dummy variable for the purposes of integration, and

$$I = I_0 \frac{A(1-m) - B\ln(m)}{A(1-m_0) - B\ln(m_0)} \quad (C-6)$$

Unfortunately, the integral (C-5) can only be solved numerically. However, various related results can be obtained from the above equations.

Let us first consider the latent image at the top of the resist  $m_0(x)$ . To determine the slope one need only differentiate equation (C-4) with respect to  $x$ . After some algebra, one obtains

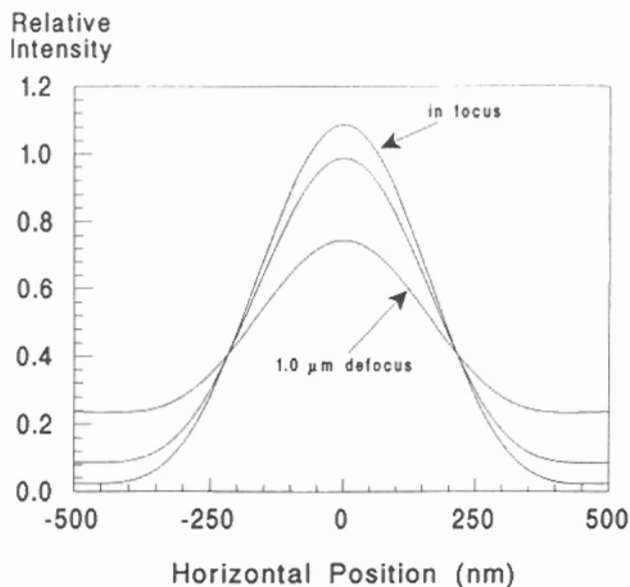
$$\frac{\partial m_0}{\partial x} = m_0 \ln(m_0) \frac{\partial \ln(I_0)}{\partial x} \quad (C-7)$$

Several very interesting and important conclusions can be drawn from this simple equation. First, the slope of the latent image is not proportional to the slope of the aerial image, but to the slope of the log-aerial image. This dependency has been discussed previously<sup>16</sup> and will be shown to be important in nearly every aspect of lithographic imaging. Further, for a given aerial image, the slope of the latent image is a function of exposure. By plotting  $m_0 \ln(m_0)$ , one can see that there is one value of  $m_0$  which gives a maximum latent image slope (Figure 8). It is easily determined that the maximum occurs at

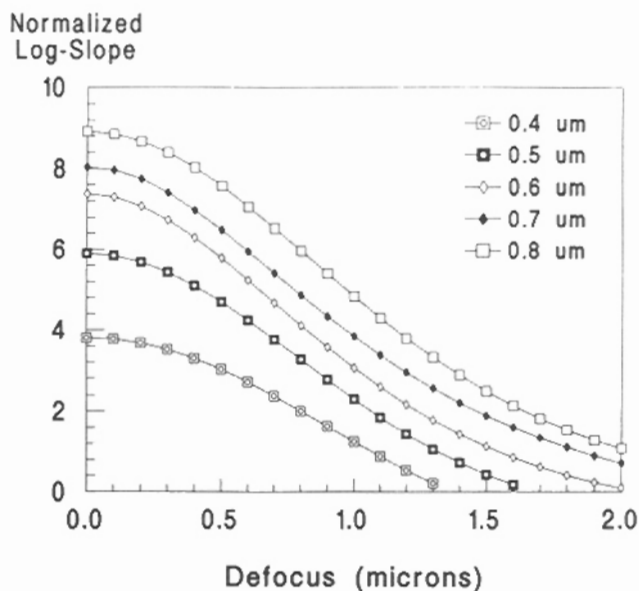
$$m_0 = e^{-1} \approx 0.37 \quad (C-8)$$

Thus, there is only one exposure energy which will maximize the latent image slope at some position  $x$  (e.g., at the mask edge), that which gives  $m_0(x)$  equal to 0.37. The implications of this result are very important. First, there is one and only one exposure energy which gives the optimum latent image. Since, as will be shown later, process latitude is a function of the latent image slope, varying the exposure will vary the latitude of a photolithographic process.

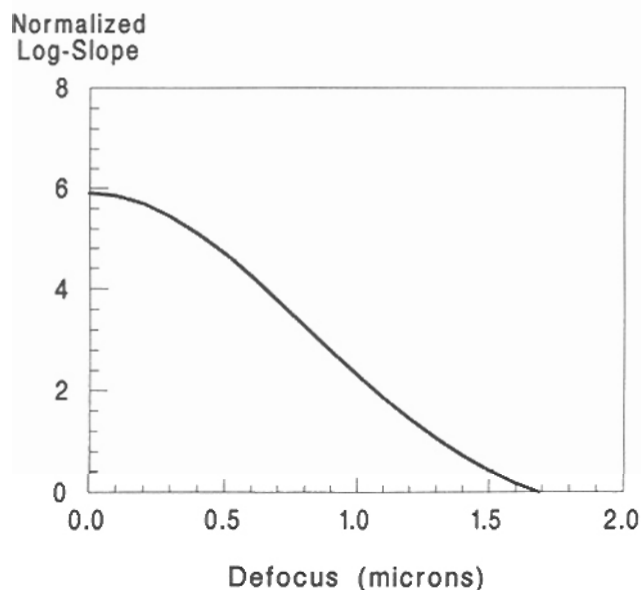
3. J. M. Shaw, M. A. Frisch, and F. H. Dill, "Thermal Analysis of Positive Photoresist Films by Mass Spectrometry," *IBM J. Res. Dev.*, Vol. 21 (May, 1977), pp. 219-226.
4. F. H. Dill, et al., "Characterization of Positive Photoresist," *IEEE Trans. Electron Dev.*, Vol. ED-22, No. 7, (Jul., 1975) pp. 445-452.
5. C. A. Mack, "Absorption and Exposure in Positive Photoresist," *Applied Optics*, Vol. 27, No. 23 (1 Dec. 1988) pp. 4913-4919.
6. C. A. Mack, "Understanding Focus Effects in Submicron Optical Lithography," *Optical/Laser Microlithography, Proc.*, SPIE Vol. 922 (1988) pp. 135-148, and *Optical Engineering*, Vol. 27, No. 12 (Dec. 1988) pp. 1093-1100.
7. C. A. Mack, "Comments on 'Understanding Focus Effects in Submicrometer Optical Lithography'," *Optical Engineering*, Vol. 29, No. 3 (Mar. 1990) p. 252.
8. C. A. Mack and P. M. Kaufman, "Understanding Focus Effects in Submicron Optical Lithography, part 2: Photoresist effects," *Optical/Laser Microlithography II, Proc.*, SPIE Vol. 1088 (1989) pp. 304-323.
9. C. A. Mack, "Understanding Focus Effects in Submicron Optical Lithography, part 3: Methods for Depth-of-Focus Improvement," *Optical/Laser Microlithography V, Proc.*, SPIE Vol. 1674 (1992) pp. 272-284.
10. M. D. Levenson, D. S. Goodman, S. Lindsey, P. W. Bayer, and H. A. E. Santini, "The Phase-Shifting Mask II: Imaging Simulations and Submicrometer Resist Exposures," *IEEE Trans. Electron Devices*, Vol. ED-31, No. 6 (June 1984) pp. 753-763
11. H. J. Levinson and W. H. Arnold, "Focus: the critical parameter for submicron lithography," *Jour. Vac. Sci. Tech.*, B5(1), (1987) pp. 293-298.
12. W. H. Arnold and H. J. Levinson, "Focus: the critical parameter for submicron optical lithography: Part 2," *Optical Microlithography VI, Proc.*, SPIE Vol. 772 (1987) pp. 21-34.
13. C. A. Mack, "Algorithm for Optimizing Stepper Performance Through Image Manipulation," *Optical/Laser Microlithography III, Proc.*, SPIE Vol. 1264 (1990) pp. 71-82.
14. C. A. Mack and J. E. Connors, "Fundamental Differences Between Positive and Negative Tone Imaging," *Optical/Laser Microlithography V, Proc.*, SPIE Vol. 1674 (1992) pp. 328-338, and *Microlithography World*, Vol. 1, No. 3 (Jul/Aug 1992) pp. 17-22.
15. C. A. Mack, "Optimization of the Spatial Properties of Illumination," *Optical/Laser Microlithography VI, Proc.*, SPIE Vol. 1927 (1993).
16. C. A. Mack, A. Stephanakis, R. Hershel, "Lumped Parameter Model of the Photolithographic Process," *Kodak Microelectronics Seminar, Proc.*, (1986) pp. 228-238.
17. F. Hurter and V. C. Driffield, "Photo-chemical Investigations of a New Method of Determination of the Sensitivity of Photographic Plates," *J. Soc. Chem. Ind.* (May 31, 1890) pp. 455-469.
18. C. A. Mack, "Lithographic Optimization Using Photoresist Contrast," *KTI Microlithography Seminar, Proc.*, (1990) pp. 1-12, and *Microelectronics Manufacturing Technology*, Vol. 14, No. 1 (Jan. 1991) pp. 36-42.
19. S. V. Babu and E. Barouch, "Exact Solution of Dill's Model Equations for Positive Photoresist Kinetics," *IEEE Electron Device Lett.*, Vol. EDL-7, No. 4 (Apr., 1986) pp. 252-253.
20. C. A. Mack, "Dispelling the Myths about Dyed Photoresist," *Solid State Technology*, Vol. 31, No. 1 (Jan. 1988) pp. 125-130.



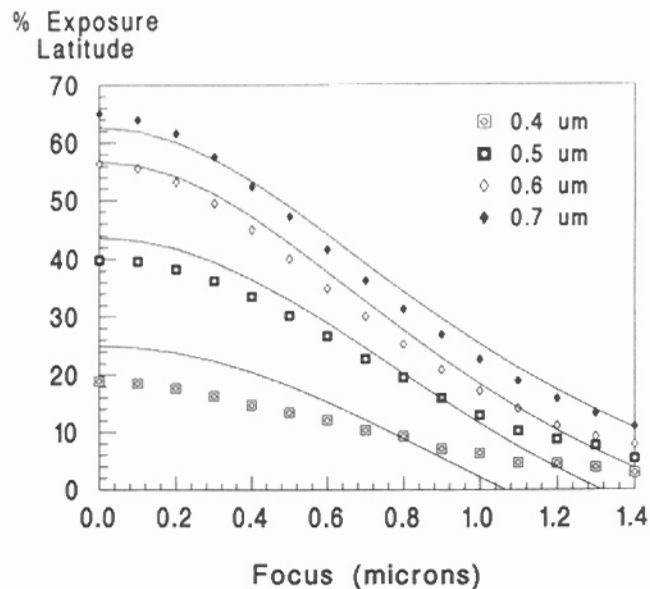
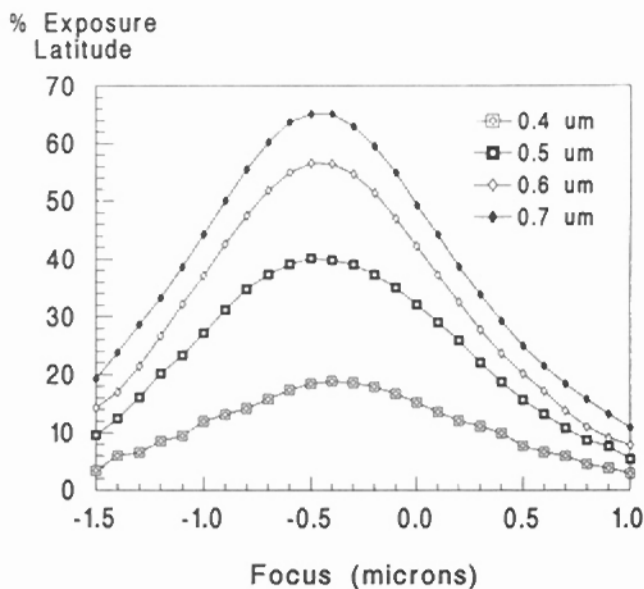
**Figure 1.** The effect of defocus on an aerial image (0.5μm lines and spaces, NA = 0.53, i-line,  $\sigma = 0.5$ , defocus values of 0, 0.5μm and 1.0μm) simulated with PROLITH/2.



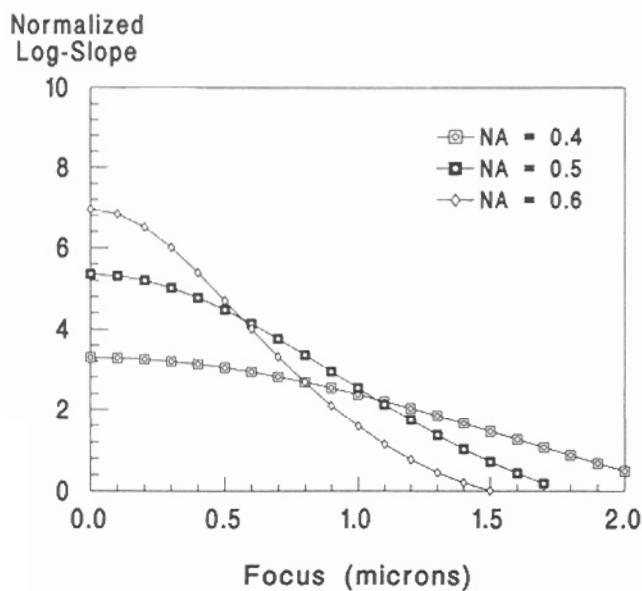
**Figure 3.** Log-slope defocus curves showing the effect of linewidth (equal lines and spaces, NA = 0.53, i-line,  $\sigma = 0.5$ ).



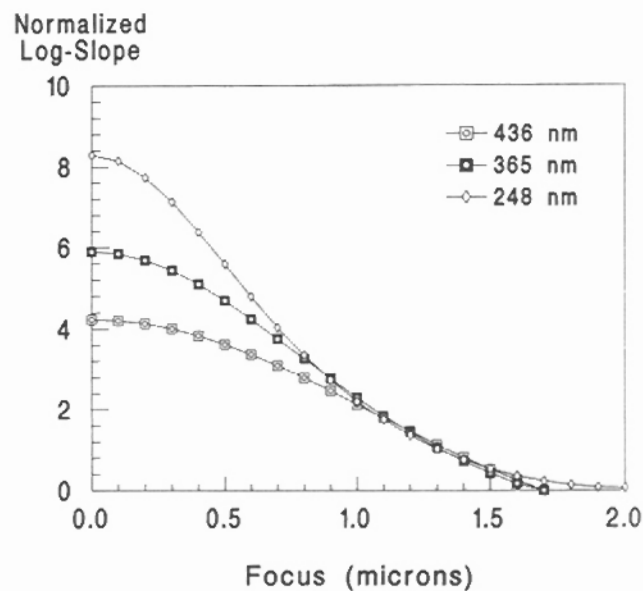
**Figure 2.** An example of the log-slope defocus curve (0.5μm lines and spaces, NA = 0.53, i-line,  $\sigma = 0.5$ ).



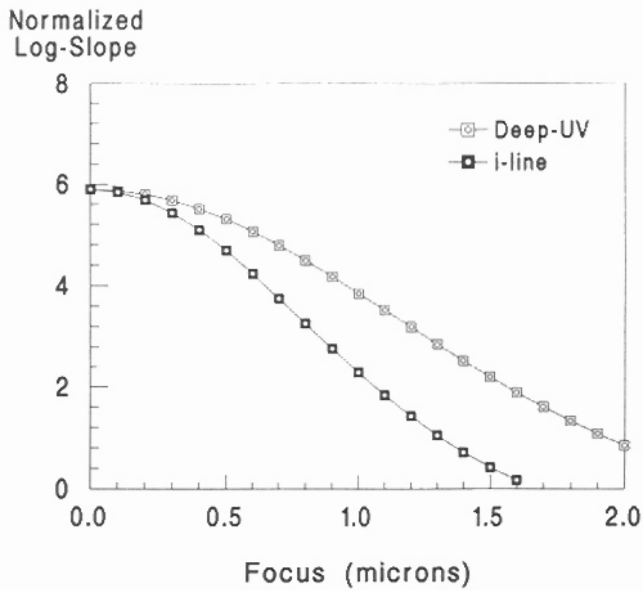
**Figure 4.** Comparing exposure latitude with image log-slope: a) simulated exposure latitude versus defocus for different linewidths, and b) comparison of the exposure latitude data (points) with the scaled NLS (lines) using  $\alpha = 8.1$  and  $\beta = 1.1$ . For a), focus is defined relative to the top of the resist, with positive focus meaning focusing above the resist. In b), best focus is set to zero for easier comparison with the log-slope curves.



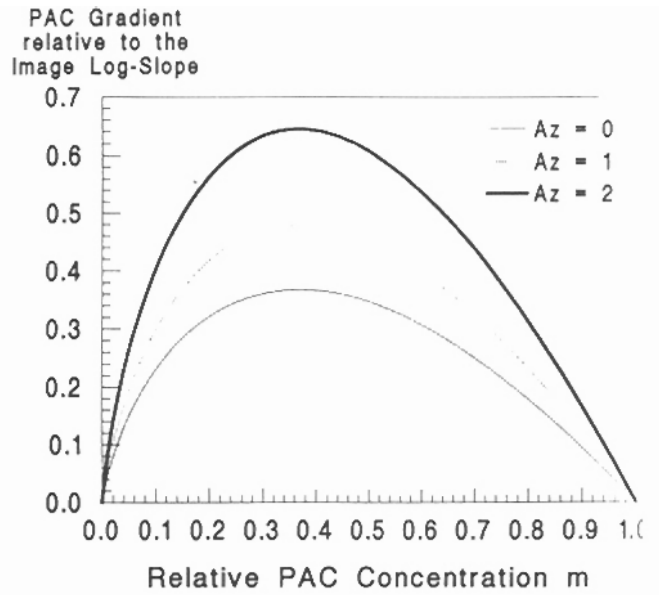
**Figure 5.** Effect of numerical aperture (NA) on the log-slope defocus curve (0.5 $\mu$ m lines and spaces, i-line,  $\sigma = 0.5$ ).



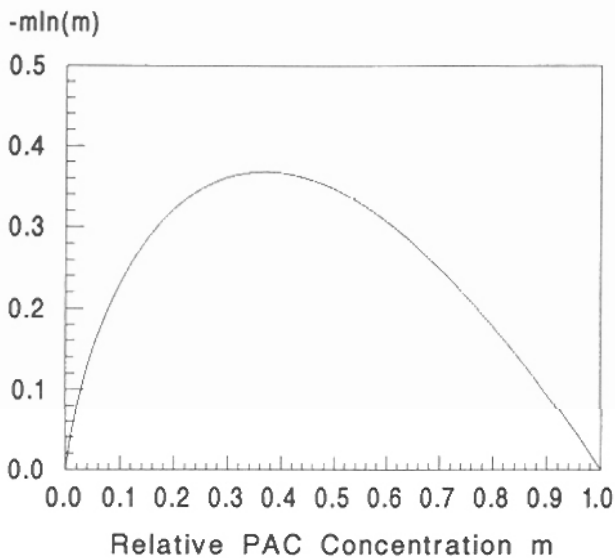
**Figure 6.** Effect of wavelength on the log-slope defocus curve (0.5 $\mu$ m lines and spaces, NA = 0.53,  $\sigma = 0.5$ ).



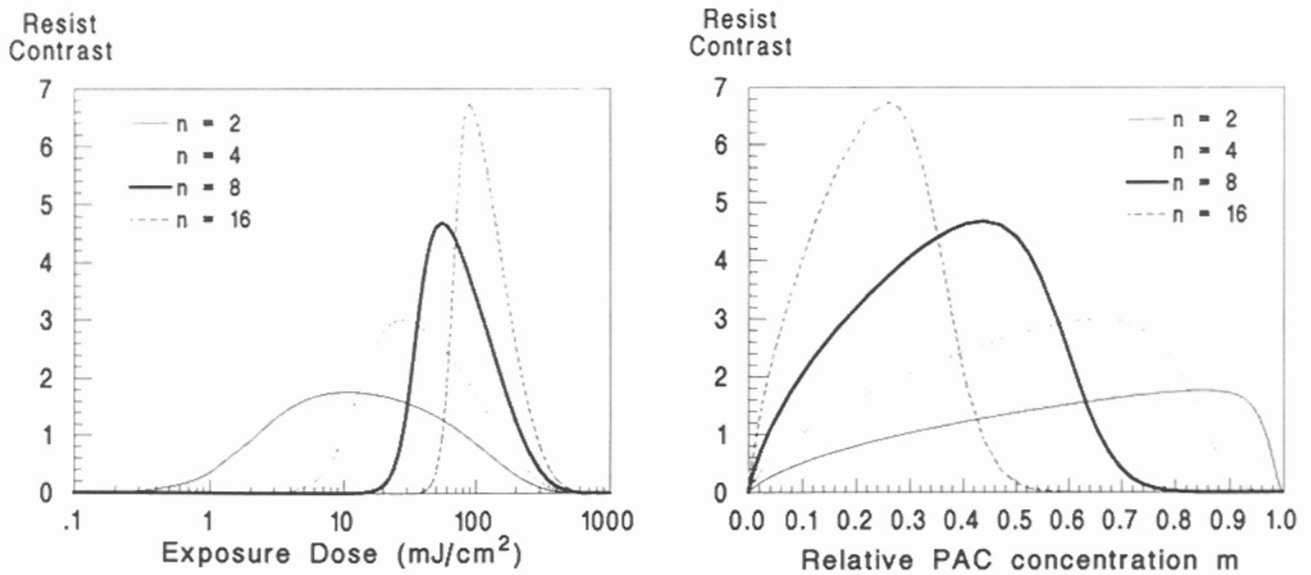
**Figure 7.** Comparison of two printers with the same value of  $\lambda/NA$  show that they have different practical resolutions ( $0.5\mu\text{m}$  lines and spaces,  $\sigma = 0.5$ . Deep UV:  $\lambda = 248\text{nm}$ ,  $NA = 0.36$ , I-Line:  $\lambda = 365\text{ nm}$ ,  $NA = 0.53$ ).



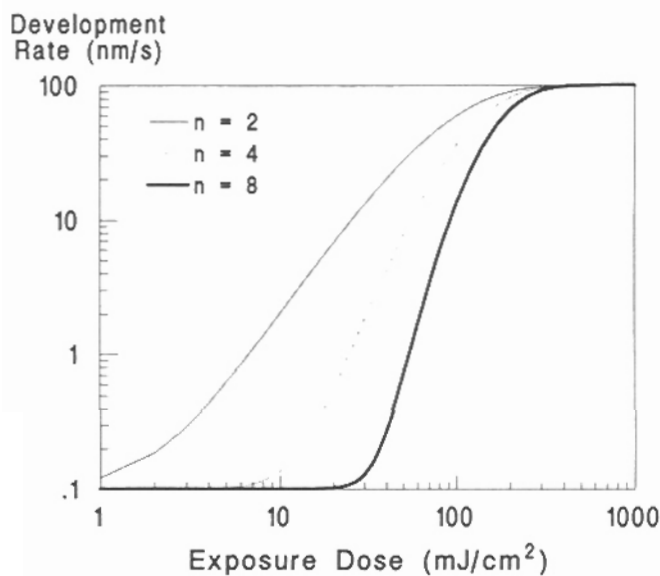
**Figure 9.** Changes in the PAC latent image slope with varying amounts of bleaching illustrates the reason for the photoresist “built-in contrast enhancement effect.”



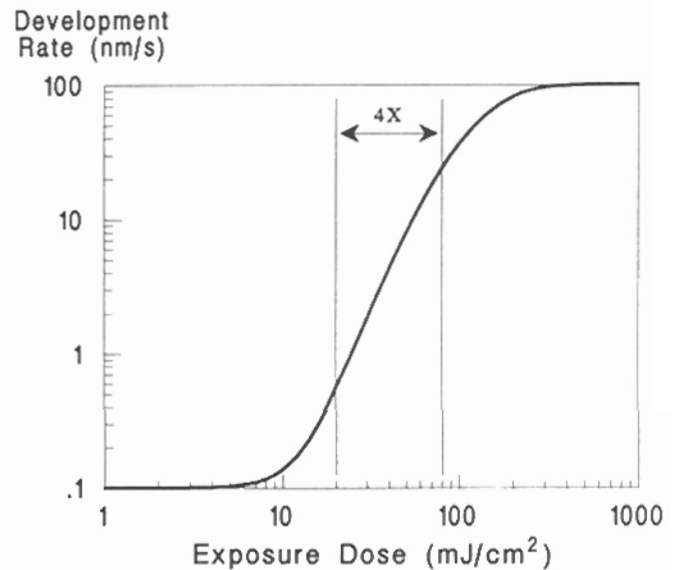
**Figure 8.** Variation of latent image slope with PAC concentration at the top of the resist (or for a non-bleaching resist) shows a clear maximum at one level of exposure.



**Figure 10.** The influence of the level of exposure on the photoresist contrast for different resist dissolution selectivity parameters  $n$  plotted a) as a function of exposure dose, and b) as a function of the relative PAC concentration. ( $R_{max} = 100$  nm/s,  $R_{min} = 0.1$  nm/s)



**Figure 11.** Typical photoresist contrast curves using the development rate versus exposure dose form of the contrast curve ( $R_{max} = 100$  nm/s,  $R_{min} = 0.1$  nm/s).



**Figure 12.** Simple path optimization scheme in which a 4X range in exposure dose is shifted along the exposure axis to give the maximum range (ratio of high to low) of development rate.